REVIEW OF SPECTROFLUORIMETRIC METHODS FOR THE DETERMINATION OF COPPER, NICKEL AND ZINC

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In this review, the literature for the reagents for the spectrofluorimetric determination of copper (references 1-47), nickel (references 48-53) and zinc (references 54-97) have been surveyed from 1986-2002. The information has been given in tabular form under the following headings: names of the reagents, $\lambda_{\text{excitation}}/\lambda_{\text{emission}}$ (wherever available), optimum pH (wherever available), remarks and references. Under the 'remarks', information regarding composition of the complex, details of the method, interferences, application of the method etc. is summarized.

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
1.	1,10-Phenanthroline	-	basic	-	The complex formed between copper (II) and 1,10-phenanthroline in an alkaline medium catalytically oxidizes H_2O_2 to super oxide radical anion, which reacts with 1,10-phenanthroline to emit chemiluminescence. The phenomenon in which chemiluminescence is enhanced in micelle solution of cationic surfactant was applied to the determination of trace amounts of copper (II). In this study, hexadecylethyldimethylammonium bromide was used as the cationic surfactant and tetraethylenepentamine was added to the mixed reagent solution to reduce the background chemiluminescent due to copper (II) impurity in reagents. The relation between logarithmic chemiluminescence response and logarithmic copper concentration was linear in the range 6.3×10^{-11} M to 1.6×10^{-10} M. Variation coefficient was 1.7 % for ten repeated determinations of $20 \mu\text{dm}^3$ of 40×10^{-10} M copper solution. Thirty determinations could be performed within 10 minutes. Interferences by other ions could be	1

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					neglected. The present method was applied to the determination of copper (II) in tap water.	
2.	1,10-Phenanthroline & cetyltrimethyl ammonium bromide.		-	8×10^{-3} ng/cm ³	Copper (II) and cetyltrimethylammonium bromide (CTMAB) enhance the Co (II)-catalysed chemiluminescence reaction of 1,10-phenanthroline and H ₂ O ₂ . The optimum reaction conditions were studied. The log-log calibration graph for copper (II) is linear from 1×10^{-10} g/cm ³ to 4×10^{-8} g/cm ³ . The detection limit of this method is 8×10^{-12} g/cm ³ copper (I) (100 μ dm ³ sample injection) and the relative standard deviation is 0.9%, 10^{-8} g/cm ³ copper (II). This method has been applied to the determination of copper (II) in natural water and human hair.	2
3.	5-Phenylazo-8-aminoquinoline	320 nm/ 365 nm	10-11	-	Trace copper (II) was determined in highly pure lead and aluminium by measuring the fluorescence at 320 nm (excitation) 365 nm (emission) of the complex formed with 5-phenylazo-8-aminoquinoline in pH 10-11 borax buffer. The fluorescence of the complex was linear in the	3

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					copper (II) concentration range of 0.5-7.0 $\mu\text{g}/50 \text{ cm}^3$. The recovery of copper (II) was 95%.	
4.	8-amino-1-naphthalene sulphonic acid (ANS)	-	-	4.7 ng/cm^3	A new method for the determination of copper in natural waters is based on fluorescence quenching and uses 8-amino-1-naphthalene sulphonic acid (ANS) as a fluorescent probe. The ANS can be combined with polyethylenediamine to increase the quantum efficiency of fluorescence. Copper reacts with polyethyleneimine to form a strong complex. ANS can be bound to cationic copper-polyethyleneimine polymer as an ion pair. The method uses sulfhydryl cotton fibres for separation and preconcentration. The detection limit is 4.7 ppb. The relative standard error is $\leq 2.0\%$. The determination range is 5-100 ppb.	4
5.	Indigo carmine- H_2O_2	-	basic	0.3 ng/cm^3	A new method based on indigo carmine- H_2O_2 chemiluminescent reaction in alkaline medium for the determination of trace copper(II) is reported. The detection limit is 0.3 $\mu\text{g Cu}/\text{dm}^3$. The linear range of the calibration curve is 10-200 $\mu\text{g Cu}/\text{dm}^3$.	5

S No	Name of the Reagents	$\lambda_{\text{ex}} / \lambda_{\text{em}}$	pH	Detection Limit	Remarks	Ref
6.	Sodium 8-amino quinoline-5-azo-p-phenylsulphonate (AQAPS)	325 nm / 370 nm	basic	-	<p>Among 30 foreign ions tested, Fe (II) and Cr (III) interfere with the determination.</p> <p>This reagent was prepared by reacting 8-aminoquinoline with diazotized p-aminophenylsulphonic acid in acid medium. The product was checked by elemental analysis, IR, thermogravimetry and paper chromatography. AQAPS reacts with copper (II) in basic medium to form a pale red product with an intense fluorescence at $\lambda_{\text{ex}}/\lambda_{\text{em}} = 325 \text{ nm} / 370 \text{ nm}$. The fluorescence intensity is proportional to copper (II) concentration in the range of 6-100 ppb and 60-250 ppb. The method was applied to the determination of trace copper (II) in pure lead and aluminium. AQAPS reacts with Pd (II) to form a blue complex, which exhibits an absorptivity of $8.0 \times 10^4 \text{ dm}^2/\text{mol}/\text{cm}$ at 660 nm in the presence of cetyltrimethylammonium bromide. Beer's law is obeyed in the range of 0-40 $\mu\text{g Pd}/50 \text{ cm}^3$. The method was applied to the determination of trace Pd (II) in catalyst secondary anode slime and</p>	6

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
7.	5-(p-Hydroxyphenyl) azo-yl-8-amino quinoline, 5-(p-chloro phenyl) azo-yl-8-amino quinoline, 5-(p-bromo phenyl) azo-yl-8-amino quinoline and 5(p-sulphonylphenyl) azo-yl-8-aminoquinoline	-	-	-	These reagents were synthesized and characterized by IR, TG, ^1H NMR and elemental analysis. Their acid dissociation constants were determined. Based on the preliminary results, these compounds could be used as fluorimetric agents for quantitative determination of metal ions as gold (II), copper (II), chromium (VI) and palladium (II).	7
8.	α , β , γ , δ -Teira (4-pyridyl) porphyrin (TpyrP)	λ_{em} : 658 nm	-	0.4 ng/cm ³	A method was developed for the determination of trace copper based on the fluorescence quenching effect of this reagent by the formation of copper (II)-TpyrP complex. The fluorimetric wavelength	8

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					of TpyrP is 658 nm. The detection limit is 0.4 ppb copper. Most of other metal ions do not interfere with the determination of copper (II) ions. The method has the advantages of high selectivity and sensitivity. It was applied to the direct determination of copper (II) in aluminium and the results were satisfactory.	
9.	Meso-tetrakis(p-sulphophenyl) porphyrin	λ_{em} : 644 nm	-	5 ng/cm ³	Micro amount of copper (II) was determined by fluorescence quenching method based on complex formation of copper (II) with this reagent. The fluorescence was measured at 644 nm. In the presence of cetyltrimethylammonium bromide and Triton X-100, the sensitivity of the proposed method is 0.005 $\mu\text{g Cu/cm}^3$. When NaF is used as a masking agent, 1 mg of Fe (II) does not interfere with the determination of copper (II). The content of copper in powdered iron, iron oxide and standard steel samples were determined with satisfactory results.	9
10.	Rhodamine B with	-	9.0	-	Copper (II) catalyses the oxidation reaction of	10

S No	Name of the Reagent	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	H_2O_2				Rhodamine B with H_2O_2 in NH_3-NH_4F medium at pH 9.0. The decolouration and decrease of fluorescence of the system is observed. The reaction can be served as a new indicator reaction for kinetic determination of trace copper by spectrophotometry or fluorimetry. The range of determination is $0.002-0.06 \mu g/25 cm^3$ by spectrophotometry and $0.001-0.05 \mu g/15 cm^3$ by fluorimetry. This method has been applied directly to the determination of copper in human hair, magnesium alloy and aluminium alloy by both spectrophotometry and fluorimetry. The relative errors are <4.0% by using both the methods.	
11.	Meso-tetrakis-(p-trimethylaminopropyl)porphyrin	-	-	$20 ng/cm^3$	The determination of the micro amount of copper by fluorescence quenching method was investigated based on the complex formation of copper (II) with meso-tetrakis(p-trimethylamino phenyl)porphyrin. The acid base equilibrium of this reagent in aqueous solution was studied. In the presence of hydroxylamine hydrochloride, the reaction is rapid and selective. Its selectivity is	11

S No	Name of the Reagents	$\lambda_{\text{ex}} / \lambda_{\text{em}}$	pH	Detection Limit	Remarks	Ref
					0.002 $\mu\text{g Cu cm}^{-3}$. When NaF is used as a masking agent, aluminium (III) (1mg) does not interfere with the determination of copper (II). The copper content in water and standard aluminium samples were determined with satisfactory results.	
12.	Luminol with H_2O_2	-	4.2	0.08 ng/cm ³	An optimized flow injection manifold for the chemiluminescence determination of cobalt (II), copper (II), iron (II) and chromium (III) by their catalytic effect on the luminol reaction with H_2O_2 is described. Detection limits are: 0.0006, 0.08, 0.3 and 0.1 ng/cm ³ respectively. The suppression effect of several carboxylic acids on the intensity is discussed. A procedure for the separation of cobalt (II), copper (II) and iron (II) on a low capacity silica based cation exchange column using 5 mM oxalic acid at pH 4.2 as the mobile phase and post column detection via the luminol reaction is also described. Detection limits for cobalt (II) and copper (II) are 0.01 and 5.0 ng/cm ³ respectively.	12
13.	Morin and H_2O_2 in	420 nm	-	-	Kinetic studies were performed on catalytic effect	13

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	EtOH-AcOEt-H ₂ O system.	548 nm			of copper (II) on oxidation of Morin by H ₂ O ₂ in a system of EtOH-AcOEt-H ₂ O under different concentrations of NH ₃ , morin, H ₂ O ₂ , ethanol and copper (II) at temperatures 15-35°C. The reaction was followed by measuring the decrease in fluorescence at 548 nm with an excitation wavelength of 420 nm. The method was applied for extractive-catalytic determination of copper (II), where it is extracted by AcOEt as an ammonium pyrolidethiocarbonate complex.	
14.	Morin with H ₂ O ₂	-	11.0 ± 0.5	1.8 ng/cm ³	A catalytic fluorimetric method was developed for the determination of trace copper based on the catalytic effect of copper oxidation of morin with H ₂ O ₂ in solution at pH 11.0 ± 0.50. The calibration graph is obtained by applying the fixed time method. The linear range of the determination is 0-12.5 ng/cm ³ for copper (II). The lower limit of determination is 1.8 ng/cm ³ . The method has been used for the determination of trace copper (II) in steel. The relative error is less than 4% for the determination of three standard steel samples.	14

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
15.	Meso-tetrakis (Trimethylammoniumphenyl) porphyrin.	-	-	2.0 ng/cm ³	Based on the fluorescence quenching of this reagent after the formation of Cu-T (4TMAP) P, a highly sensitive and selective fluorescence quenching method for the determination of copper (II) is presented. The detection limit of copper (II) was 2 ppb. It has been used satisfactorily to the direct determination of copper (II) in drinks.	15
16.	Cystamine with oxygen and luminol	-	basic	1.28 ng/cm ³	The copper (II)-catalysed oxidation of cystamine with oxygen was carried out in a basic medium involving luminol after preferential oxidation of cystamine to disulphide, a copper catalysed chemiluminescence reaction was subsequently commenced with H ₂ O ₂ accumulated during the oxidation of cystamine. Thus a delay time from reaction initiation to a sharp flash of chemiluminescence was observed. This delayed chemiluminescence of luminol was applied to the determination of copper (II) by measuring the delay time and the chemiluminescence intensity at maximum light emission were linearly corrected with the copper (II) concentration over the range from	16

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					the detection limit of 3.0×10^{-6} M to 2.0×10^{-5} M. The relative standard deviation of the chemiluminescence intensity and the delay time in 5 successive experiments was 3.0% at 1×10^{-5} M copper (II). The tolerance limits of Fe (III), Ni (II) and Zn (II) in the present method were 20-100 times higher than those in the conventional luminol chemiluminescence method.	
17.	Thiamine	-	basic	-	The reaction involving the oxidation of thiamine by copper (II) in basic solutions to fluorescent thiochrome has been adapted to the determination of thiamine by flow injection analysis. Linear calibration graphs are obtained between 0.30 and $6.02 \mu\text{g}/\text{cm}^3$ with a sampling rate of 50 samples per hour and a standard deviation of 0.53%. This reaction has also been adapted to the determination of copper (II) over the range 0.5-5.0 $\mu\text{g}/\text{cm}^3$. The applicability of both the methods for the determination of thiamine and copper is demonstrated by investigating the effect of potential interferences and by the analysis of real samples.	17

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
18.	1,10-phenanthroline and H_2O_2	-	-	<0.025 ng/cm^3	A method for dissolved copper by rapid determination in seawater is based on the formation of a complex between copper and 1,10-phenanthroline and the subsequent chemiluminescence during the oxidation of the complex by H_2O_2 . A flow injection manifold was constructed which provides for the separation of copper from the sea water matrix with a column of immobilized 8-hydroxyquinoline. The column eluent was injected in to a carrier stream, mixed with the reagents and delivered to a flow cell where emitted light was detected and used to quantify the amount of copper in the sample. The technique is noteworthy for its low detection limit (<0.4 nM), the rapidity of sample processing (~8 minutes/sample), small sample volumes required (~4 cm^3), and the minimal precautions necessary for the prevention of sample contamination during shipboard processing.	18
19.	Luminal with KCN	-	-	0.001 ng/cm^3	Trace copper was determined using the flow injection chemiluminescence analyzer developed in	19

S. No	Name of the Reagents	λ ex / λ em	pH	Detection Limit	Remarks	Ref
					the author's laboratory based on the reaction of luminol, KCN and copper (II). The analyzer consists of a coil chemiluminescence flow cell, a photo multiplier, an amplifier and a recording system. The chemiluminescence is linear for copper (II) concentration in the range of 4×10^{-10} to 8×10^{-7} mg/cm ³ . The detection limit is 1×10^{-11} g/cm ³ of copper. Copper was determined in natural water with satisfactory results.	
20.	Luminol and H ₂ O ₂ by CAR technique.	-	-	-	The chemiluminescence reaction between luminol and H ₂ O ₂ in the presence of copper (II) was used to assess the potential of the continuous addition of the reagent (CAR) technique for chemiluminescence determinations. This approach allows this type of reaction to be studied in terms of reaction rate. So maximum reaction rate measurements can be compared with classical peak height measurements. The reaction rate method provided better analytical features in the chemiluminescence determinations of copper (II): dynamic range 1-700 ng/cm ³ ; precision (relative	20

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
21.	Thiamine	-	basic	0.25 ng/cm ³	standard deviation) ~3%; sample throughput 48 samples h ⁻¹ . This technique facilitates thorough, reproducible mixing of sample and reagents, in addition to recording the whole chemiluminescence response curve and altering the rate of the chemiluminescence process which can be monitored with a straightforward data acquisition system.	21
22.	p-Hydroxy benzylidene-5-(8-quinolylazo)-8-aminoquinoline (HBQAAQ)	-	basic	1.0 ng/cm ³	A new fluorimetric method for the determination of micro amounts of copper was set up based on the oxidation of thiamine into highly fluorescent thiochrome by copper (II) in basic medium. The fluorescent intensity was linear with the concentration of copper from 0.006 to 10 ng/25cm ³ . The relative standard deviation was 3.5% and the detection limit was 0.25 ng/cm ³ . The method has been used to determine copper in pure aluminium and hair samples.	22

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	quinolyazo)-8-aminoquinoline (HBQAAQ)				synthesized as a fluorescent agent. The reagent reacts with copper (II) to form a stable complex to cause the quenching of fluorescence in the neutral to weak alkali media. The complex showed a copper (II) to HBQAAQ molar ratio 1:2, a detection limit 1.0 ng/cm^3 and a linear detection range of $0-0.5 \text{ } \mu\text{g}/10 \text{ cm}^3$. The method was used for the determination of copper in water and chemical reagent samples with satisfactory results.	23
23.	Fluorescein	-	basic	0.5 ng/cm^3	A novel chemiluminescence system, fluorescein - $\text{NH}_2\text{-OH}\cdot\text{OH}^-$, was developed for the determination of copper (II) in serum. A weak light emission arises from hydroxylamine in the presence of the organic reagent fluorescein in basic aqueous solution under the conditions of $1 \times 10^{-3} \text{ mol/dm}^3$ NH_2OH and $5 \times 10^{-3} \text{ mol/dm}^3$ fluorescein. The light intensity is linearly dependent upon the concentration of copper (II) within the range 1-20 ppb. The relative standard deviation of the determination of copper (II) is 4.2% ($n=13$) and the detection limit is 0.5 ppb. The system is highly	

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24.	Bis(salicylaldehyde) Tetraamethylethylenediamine (H ₂ SA ₂ Ten).	370 nm / 440 nm	-	-	<p>selective for copper except in the presence of iron (II, III) and cobalt (II). In conjunction with potassium fluoride as masking agent, the method was successfully applied to the determination of micro amounts of copper (II) in serum. A mechanistic study of the chemiluminescence reaction is also discussed.</p> <p>The reagent, H₂SA₂Ten and its copper (II), nickel (II), palladium (II), cobalt (II) and oxovanadium (IV) complexes indicate fluorescence in visible region. The conditions for the fluorimetric determination of metals as metal chelate compounds were optimized. The linear calibrations were obtained at 0-50 $\mu\text{g}/\text{cm}^3$ of a complex in CHCl₃. Solvent extraction procedure was developed for the fluorimetric determination of copper in toluene. The excitation and emission wavelengths were 370 nm and 440 nm respectively. A linear calibration curve was obtained with 0-2 $\mu\text{g}/\text{cm}^3$ copper in toluene. The copper in copper wires were determined and were found 79.6%(cv</p>	24

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					2.5%) as compared to 82% (cv 0.8%) using a omic absorption.	
25.	Bis[4-(α -naphthylazo)salicylidene]-o-phenylene dimine (BNASPD)	λ_{em} : 435 nm	-	1.0 ng/cm ³	A new fluorescent reagent bis[4-(α -naphthylazo)salicylidene]-o-phenylenediamine (BNASPD) was synthesized. The reagent exhibited fluorescence emission at 435 nm. The reaction could form a complex with copper ion to cause its fluorescence quenching. The reaction showed high selectivity and sensitivity for copper. A new spectrofluorimetric method for the determination of trace copper using this reagent was developed. The detection limit for copper is 1.0 ng/cm ³ . The method was used to determine trace copper in inorganic chemicals and mineral water samples with satisfactory results.	25
26.	N-Methyl-anthranilic acid (NMAA)	-	-	-	The effect of cations like Na (I), K (I), Cd (II), Cu (II), Ag (I), Zn (II), Co (II), Ni (II), Pb (II), Fe (II), Al (III) and Cr (III) on the fluorescence intensity of NMAA was studied. All the cations studied with the exception of Na (I) and K (I) caused an	

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27.	Bis(salicyl-aldehyde) Tetramethyl-ethylenediamine (H ₂ SA ₂ Ten) on HPLC column	-	-	-	<p>enhancement in the fluorescent intensity of NMAA Based on the fluorescent effect, these cations were divided into three groups. The fluorescence enhancement phenomenon was used for the spectrofluorimetric determination of these cations in aqueous samples. Limit of detection for each cation was also studied and reported.</p> <p>Copper (II), nickel (II), palladium (II) and oxovanadium (IV) chelates of this reagent were separated on normal phase HPLC column Si 100, 5μ. The chelates were eluted with a ternary mixtures of 1,2-dichloroethane: chloroform: acetonitrile (70:28:2), vol/vol/vol). The detection was achieved using a spectrofluorimetric detector. The linear calibration ranges for each of the complexes at optimized spectrofluorimetric detection were determined. A solvent extraction procedure in chloroform was examined for the determination of nickel and this method was applied to the estimation of nickel in a nickel-aluminium alloy.</p>	27

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28.	3-p-Tolyl-5-(2'-carboxyphenylazo) rhodanine (PMPRACP)	305 nm / 400 nm	5.6	-	A new fluorescent reagent, 3-p-tolyl-5-(2'-carboxyphenylazo) rhodanine was synthesized and elemental analysis, IR, ¹ HNMR and MS confirmed its structure. A fluorescence analytical method for copper (II) was developed based on the reaction of copper (II) with PMPRACP to form a fluorescent complex with $\lambda_{ex}/\lambda_{em}$ is 305-nm/400 nm at pH 5.6. The linear relationship between the fluorescence intensity and concentration of copper (II) was 0-1.6 $\mu\text{g}/25\text{ cm}^3$ and the detection limit was $5 \times 10^{-4} \mu\text{g}/\text{cm}^3$. The method was applied to the determination of trace copper in cocoon, natural silk and silk cloth with satisfactory results.	28
29.	Calcein Blue (CB)	365 nm / 447 nm	4.5	-	A method of fluorescence quenching was used for the rapid determination of copper in steel. Copper reacts with calcein blue (CB) to form a stable complex, which can quench the fluorescence of CB in acetic acid-sodium acetate buffer at pH 4.5. The maximum excitation wavelength and the maximum emission wavelength of CB were 366 nm and 447 nm respectively. The linear range was 0-1.0 $\mu\text{g}/10$	29

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					cm ³ for copper (II). The method is rapid and simple. It was applied to the determination of copper in steels with satisfactory results.	
30.	Salicylaldehyde benzaldehydezone	300 nm / 410 nm	9.0	12.4 ng/cm ³	A new fluorimetric reagent salicylaldehydebenzaldehydezone was established. The fluorimetric reaction of the reagent with copper was carried out in aqueous medium at pH 9.0 and studied. The fluorescence excitation and emission wavelengths of the complex are 300 nm and 410 nm respectively. The linear range is 0.0-0.8 μ M/10 cm ³ , the detection limit is 12.4 ng/cm ³ and the molar ratio of copper to the reagent is 1:1. The method was applied to the determination of trace copper in tea and hair with satisfactory results.	30
31.	Salicylidene-5-(8-quinolylazo)-8-amino quinoline (SQAAR)	-	neutral	1.0 μ g/dm ³	The reagent SQAAR was synthesized and used for the determination of trace copper. The formation of a stable complex of SQAAR with copper (II) in neutral or weak alkaline media can quench the fluorescence of SQAAR. The detection limit was 1.0 μ g/dm ³ . Up to 20 cations and anions did not	31

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
32.	7-(8-hydroxy-3, 6-di-sulpho- capthylazo)-8-hydroxyquinoline-5-sulphonic acid.	-	-	-	interfere with the determination of copper in mineral water and inorganic chemicals. A new catalytic fluorescence determination of trace copper (II) was established by using 7-(8-hydroxy-3, 6-disulphonaphthylazo)-8-hydroxyquinoline-5-sulphonic acid and the experimental conditions were optimized by multi object; punish function simplex method, they are 0.05% reagent 1.3 cm^3 , $0.1 \text{ mol/cm}^3 \text{ NaOH}$ 6.2 cm^3 , $0.1\% \text{ KIO}_4$ 1.6 cm^3 and time 15 minutes. The mechanism of the reaction was studied. The method is applied to the determination of trace Cu (II) in water sample and alloy samples with satisfactory results.	32
33.	N-Dansyl-N'-ethylthiourea (DET)	-	-	-	DET forms fluorescent chelates with a large number of heavy metal ions. The influence of the pH value on the luminescence of DET causes a bathochromic shift of the emission maximum which is linearly dependent on the copper (II) concentration. Low detection limits and a wide	33

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
34.	Indigo Carmine- H_2O_2	-	-	20.0 ng/cm ³	linear range of detection are achieved by HPLC using RP-18 columns as stationary phase. Also presented are measurements of fluorescence decay times of the ligand as well as some complexes.	34
					A post-column reaction chemiluminescence detection method in chromatography is described. The chemiluminescence system was indigo-carmine-hydrogen peroxide. The chemiluminescence reaction conditions and the separation conditions of cobalt and copper in chromatography are presented. The detection limits were 1.0 and 2.0×10^{-8} g/cm ³ for cobalt and copper respectively.	35
35.	Luminol-light green SF-peroxide-copper (II)	-	-	0.102 ng/cm ³	A chemiluminescence system of luminol-light green SF-peroxide-copper(II) was reported. A method for the determination of micro amount of copper by using the system was proposed. The detection limit was 1.6×10^{-9} mol/dm ³ and the RSD was 2.4%. The method was applied to the	

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36.	Rhodamine 800 in Nafion 117 polymer	-	-	-	determination of copper (II) in hair, tea and copper ores with satisfactory results. The fluorescence quenching and anisotropy measurements of the neat-IR dye Rhodamine 800 in Nafion 117 polymer are reported using ps diode laser excitation. Unlike cabocyanine dyes used previously, this sensor was photochemically stable in the Nafion and ideal for the selective detection of copper (II) ions, because of the large overlap of the fluorescence spectra and the absorption spectra of copper. The quenching of Rhodamine 800 by other transition metal ions is insignificant in comparison to copper. Anisotropy studies imply that the rhodamine 800 is located in the water-polymer interface. The quenching was shown of another Xanthene dye Rhodamine 6G by copper ions in Nafion using 2 photon excitation from a regeneratively amplified fsTi: Sapphire laser.	36
37.	Cu (II)-Tb-TMA-Triton X-100.	-	-	-	A fluorescence quenching system of copper (II)-Tb-TMA-Triton X-100 was established for the	37

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
	(TMA-Benzene-1,3,5-tricarboxylic acid)				determination of copper (II). The fluorescence intensity of the determination system is linear in the concentration range of 1.58×10^{-7} to 2.83×10^{-5} mole/dm ³ copper(II). The proposed method was applied to the determination of copper(II) contained in various copper ores with satisfactory results.	
38.	Luminol-MnO ₄ ⁻	-	basic	-	A method was developed on the basis of inhibition effect of copper on luminol-MnO ₄ ⁻ chemiluminescence system. Luminol and MnO ₄ ⁻ were immobilized on the D201x7 cationic exchange column. The chemiluminescence of the NaOH solution from eluting luminol and MnO ₄ ⁻ were measured for determining copper quantity. Copper was determined in hair samples with satisfactory results.	38
39.	Rhodamine 800; Texas Red X and N, N, N', N'-tetramethylethylenediamine	-	-	~2.0 ng/cm ³	Two kinds of fluorescence lifetime sensors for copper (II) ions based on energy transfer are presented. The previously developed sensor with near IR donor Rhodamine 800 and copper (II) ion as acceptor is compared with a new system based	39

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
40.	Eu-Terpyridine-poly aminopoly carboxylate	-	-	7.0 ng/cm ³	<p>on Texas Red X as the donor and N, N, N', N'-teramethylethylenediamine :copper (II) complex as acceptor. Enhanced absorption spectra of the ligand: copper (II) complex increases the rate of energy transfer which improves detection limit for copper concentration in water down to ~2 ppb.</p> <p>This work describes a novel assay for copper at trace levels. Aqueous copper (II) ions efficiently quench the luminescence of a Eu-terpyridine-polyaminopolycarboxylate chelate. Both static and dynamic quenchings were identified and separated by time-resolved luminous spectroscopy. Single experimental decay observed throughout with decay time ranging from 1261 μs at 300 ng/cm³ copper, reflecting strong dynamic quenching. The calibration graph obeys the Stern-Volmer equation and is given for the 0-300-ng/cm³ ranges. The quenching constant was determined at 1.39×10^5 dm³/mol and the 3 SD limit of detection was 7.0 ng/cm³. Time resolved luminous spectroscopy provided additional selectivity for copper by</p>	40

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
41.	5-(3-Fluoro-4-chloro phenylazo)-8-benzene sulphonamidoquinoline (FCPBSQ), 5-(3-fluoro-4-chloro-phenyl azo)-8-aminquinoline (FCPAQ) and 4,4'-bis(8-aminoquinoline-5-azo)-	-	basic	0.80, 0.20 and 0.50 $\mu\text{g}/\text{cm}^3$	discriminating static quenching by other heavy metals. Thus, solely static quenchers Zn (II), Cd (II), Hg (II) and Pb (II) did not interfere, whereas the relative interferences by dynamic quenchers was 0.16% Fe (III), 1.15% Co (II), 0.38% Ni (II), 3.81% Cr (II) and 3.03% Mn (II). The quenching mechanism is discussed. The method appears suitable for industrial and environmental applications.	41

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	biphenyl (BAQABP)				methods were successfully applied to the determination of trace amount of copper in ores, alloys, water and hair samples.	
42.	8-Amino-quinoline-5-azo derivatives.	284 nm /380 nm	7.2-8.8	0.04 ng/cm ³	Three 8-aminoquinoline-5-azo derivatives were synthesized with o-aminophenylarsonic acid and 8-aminoquinoline as raw materials and are characterized by TLC, elemental analysis and IR. A method for the determination of copper (II) was presented based on the fluorimetric reaction of copper (II) with 5-(2-arsenophenylazo)-8-aminoquinoline (o-APAQ). A yellowish complex was formed with copper (II) and the reagent in pH 7.2-8.8. H ₃ BO ₃ -KCl-NaOH buffer solution. The complex had an intense fluorescence at $\lambda_{em}/\lambda_{ex}$ = 380 nm/284 nm, linear range 0-15 ng/cm ³ and the detection limit is 0.04 ng/cm ³ . The method was used in the determination of micro amount of copper in synthetic samples with the recovery of 97.4-103.6%.	42

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
43.	Luminol-H ₂ O ₂ -copper (II)-Coomassie Brilliant Blue G 250	-	-	1.5 ng/cm ³	A new reverse flow injection chemiluminescent analytical system of luminol-H ₂ O ₂ -copper (II)-Coomassie Brilliant Blue G250 is developed. The linear range for the determination of copper (II) is 0.005-0.100 mg/dm ³ and the detection limit is 0.0015 mg Cu (II)/dm ³ . The relative standard deviation (n = 10) for an analytical concentration of 0.050 mg Cu (II)/dm ³ is 3.6%. The tolerable concentration for interference ions is relatively large. The precision, accuracy and selectivity of the method are very good. This method has been used to determine trace copper (II) ions in river water with satisfactory results.	43
44.	Salicylfluorone-Cetyltrimethylammonium bromide	458 nm / 549 nm	6.3-7.0	-	The fluorescence properties and applications of copper(II)-salicylfluorone-cetyltrimethylammonium bromide fluorescent complex system were described. In the buffer solution of hexamethylenetetramine-HCl, at pH 6.3-7.0, the Cu (II)-SA 5-CTMAB fluorescent complex showed maximum excitation wavelength at 498 nm and a maximum emission wavelength at 549 nm. The	44

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					linear range was 0-1 $\mu\text{g}/25 \text{ cm}^3$. The method is very fast and highly selective. When it was tested with standard samples in the presence of masking agents, good results were obtained.	
45.	5'-Nitrosalicyl fluorone with triton X-100.	500 nm / 550 nm	10.0-11.0	0.4 $\mu\text{g}/\text{dm}^3$	The determination of trace copper was studied with 5'-nitrosalicylfluorone fluorescence quenching method. A ternary complex of copper (II), 5'-nitrosalicylfluorone and Triton X-100 was formed in $\text{Na}_2\text{B}_4\text{O}_7\text{-NaOH}$ buffer solution at pH 10.0-11.0. The excitation wavelength was 500 nm; the emission wavelength was 550 nm, the linear range 0-120 $\mu\text{g}/\text{dm}^3$ and the detection limit 0.4 $\mu\text{g}/\text{dm}^3$. Potassium sodium tartrate and triethanolamine can be used as masking agents. The method was used in the determination of copper in tea, human hair, beverage and water with the RSD 1.2-4.8%. The recovery 98.0-102.4%, and the results consistent with those by AAS.	45
46.	Porphyrins-Bis(2,4,6-trichloro	-	-	0.805 ng/cm^3	Six water soluble porphyrins were examined as a sensitizer (fluorophore) in the bis(2,4,6-	46

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
	phenyl)oxalate (TCPO)-H ₂ O ₂				trichlorophenyl) oxalate system. Among the highest chemiluminescence showed the TCPO-H ₂ O ₂ -coproporphyrins III chemiluminescence intensity. The TCPO-H ₂ O ₂ -coproporphyrins III chemiluminescence system was separated and examined in each micelle solution using a non-ionic surfactant such as Brij 35 and Triton X-100 and an ionic surfactant such as cetyltrimethyl ammonium chloride (CTMAC) and sodiumdodecyl sulphate. The chemiluminescence intensity along with the coexistence of the CTMAC micelle increased ~36 times compared to that in the absence of surfactant. The quenching chemiluminescence determination of copper was established using the complex formation of coproporphyrins and copper (II). The calibration graph for the concentration of copper (II) was linear at 2×10^{-8} M to 1×10^{-6} M and the detection limit was 1.26×10^{-8} M. The relative standard deviation was 2.9% (10 determinations). This method was applied to the determination of copper in wastewater and satisfactory results were obtained.	

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
47.	4,5-Dihydroxy-1, 3-benzene- disulphonic acid (Trion)	294 nm 350 nm	8.0	25.6 ng/cm ³	A spectrophotometric method was developed for the determination of trace copper (II) in real samples with 4,5-dihydroxy-1,3-benzene-disulphonic acid (Trion) as a fluorimetric reporter. Trion is very soluble in water and is a good fluorimetric reagent. However, as trion was complexed with copper (II), the fluorescence intensity decreased proportionally to the concentration of copper (II) by a static quenching effect. The excitation wavelength and the fluorescence wavelength of trion were 294 nm and 350 nm respectively, as it was caused by a quenching effect from copper (II) at pH 8.0. The highest sensitivity was shown at trion concentration of 5.0×10^{-5} M. To enhance the quenching effect, the copper (II)-Trion complex solution was heated up to 80°C for 90 minutes. As for copper (II), the interference by Co (II) was very serious which was eliminated by oxalate ion. The linear response to copper (II) was shown at the concentration range between 5.0×10^{-7} M and 1.0×10^{-5} M. With this proposed method, the detection limit of copper (II)	47

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					was $3.83(\pm 0.09) \times 10^{-7}$ M. Recoveries of copper (II) in the diluted brass samples and stream water samples were ~100%. Based on results from experiment, this proposed technique could be applied to the practical determination of copper (II) in real samples.	
48.	1,2-Diaminocyclohexanetetracetic acid with 2-hydroxy benzaldehyde thiosemicarbazone, H_2O_2 , NH_3 and Mn (III) as catalyst and measuring the fluorescence (excitation 365 nm, emission 440 nm). The same principle can also be used for determining trace Mn (II) or Ni (II).	365 nm / 440 nm	-	-	The determination of 1,2-dichlorocyclohexanetetracetic acids involves dissolution in ethanol, addition of 2-hydroxybenzaldehyde thiosemicarbazone, H_2O_2 , NH_3 and Mn (III) as catalyst and measuring the fluorescence (excitation 365 nm, emission 440 nm). The same principle can also be used for determining trace Mn (II) or Ni (II).	48
49.	$\alpha, \beta, \gamma, \delta$ -Tetrakis(p-sulphophenyl)porphyrin(TPPS ₄) with dimethylglyoxime.	-	basic	-	Nic(II) forms a complex with $\alpha, \beta, \gamma, \delta$ -Tetrakis(p-sulphophenyl)porphyrin(TPPS ₄) by metal substitution in the Cd-TPPS ₄ complex in weakly alkaline medium containing cadmium salt and imidazole in a boiling water bath, the result led to the fluorescence quenching of TPPS ₄ and a fluorimetric method for the determination of micro	49

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					amounts of nickel (II) was established. In order to separate nickel from most interfering ions dimethylglyoxime was used for the extraction of nickel. This method has been used for the determination of nickel in steels and the results are satisfactory.	
50.	Acetone	-	-	2.5 ng/cm ³	The above one chemiluminescence determination of nickel in water was investigated. Optimization data for the determination of nickel (II) and interference data for >20 species are provided. The limit of detection for nickel (II) is 2.5 ng/cm ³ and the linear dynamic range 10 ng/cm ³ . The application of the method to the determination of nickel (II) in river water is discussed.	50
51.	Luminol-H ₂ O ₂ - Ni(OH) ₂ ²⁻ⁿ	-	-	1.0 ng/cm ³	A new solid surface chemiluminescence method for determining nickel using luminol-H ₂ O ₂ -Ni(OH) ₂ ²⁻ⁿ luminescence system is developed. The determination is based on the catalytic effect of nickel on the chemiluminescence reaction of luminol and H ₂ O ₂ . The linear range for nickel is	51

S No	Name of the Reagents	λ_{ex} λ_{em}	pH	Detection Limit	Remarks	Ref
52.	N-Methyl-anthranilic acid (NMAA)	-	-	-	<p>10.0-1000 ng. The detection limit is 1.0 ng and the relative standard deviation for 10 ng nickel is 4.3% (n = 11). The interference ions are separated by paper chromatography with acetone-HCl-H₂O as a mobile phase. The method has been successfully applied to the micro determination of nickel in the mineral and steel samples</p> <p>The effect of cations like Na (I), K (I), Cl (II), Cu (II), Ag (I), Zn (II), Co (II), Ni (II), Pb (II), Fe (II), Al (III) and Cr (III) on the fluorescence intensity of NMAA was studied. All the cations studied with the exception of Na (I) and K (I) caused an enhancement in the fluorescent intensity of NMAA. Based on the fluorescent effect, these cations were divided into three groups. The fluorescence enhancement phenomenon was used for the spectrofluorimetric determination of these cations in aqueous samples. Limit of detection for each cation was also studied and reported.</p>	25

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
53.	Bis(salicylaldehyde) tetramethylene diimine (H_2SA_2Ten)	-	-	-	Copper(II), nickel(II), palladium(II) and oxovanadium(IV) chelates of this reagent were separated on normal phase HPLC column Si 100, 5 μ . The chelates were eluted with ternary mixtures of 1,2-dichloroethane: chloroform: acetonitrile(70:28:2), (vol/vol/vol). The detection was achieved using a spectrofluorimetric detector. The linear calibration range for each of the complex at optimized spectrofluorimetric detection was determined. A solvent extraction procedure in chloroform was examined for the determination of nickel and this method was applied to the estimation of nickel in a nickel- aluminum alloy.	27
54.	Salicylfluorone (SAF)-Tween 80	-	-	-	A new selective and sensitive spectrofluorimetric method for the determination of trace nickel (II) in water and biological samples has been developed. This method is based on the quenching of fluorescence of salicylfluorone(SAF)-Tween 80 system, due to the formation of a complex Ni(II)-SAF-Tween 80. There was a linear relationship in the range of 1.0-4.0 ng/25 cm ³ for Ni(II)	52

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					determination in water samples.	
55.	Phenanthroline	272 nm/ 366 nm	-	-	A new selective and sensitive spectrofluorimetric method for the determination of trace amounts of nickel(II) in industrial wastewater has been developed. This method is based on the quenching of fluorescence of phenanthroline due to the formation of complex nickel-phenanthroline. The excitation and emission wavelengths were found to be 272 nm and 366 nm respectively. There was a linear relationship in the concentration range of 10.0-120 ng/cm ³ for nickel. This method is simple and rapid and has been applied to the determination of nickel in industrial wastewater.	53
56.	Salicylaldehyde-thiocarbonylhydrazine	-	-	-	Synchronous scanning spectrofluorimetry was used to determine mixtures of diverse metal ions at trace levels using some Schiff's bases as reagents. Between the compounds tested di-2-pyridylmethylene-2-furoylhydrazine I and salicylaldehyde-thiocarbonylhydrazine II show the most interesting results. With the reagent I Ga (III) can	54

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					be determined at concentration $2-10 \text{ ng/cm}^3$ in the presence of Al(III). Reagent (I) can be used in the simultaneous determination of Ga(III) and Zn(II) in the concentration intervals of 2-10 and 20-1500 ng/cm^3 respectively.	
57.	5,7-dichloro-2-methyl-8-hydroxyquinoline in CHCl_3	399 nm / 544 nm	7.0-9.0	-	The distribution equilibrium of the zinc complex with 5,7-dichloro-2-methyl-8-hydroxyquinoline in the water chloroform system was studied at 25°C . The influence of pH, reagent and metal concentrations and the presence of NaClO_4 in the aqueous phase were determined. The complex extracted is the simple 1:2 chelate, ZnR_2 , although at ligand concentrations higher than 0.3, the self adduct complex seems to begin to form. The extraction constant of the ZnR_2 species, refined by means of the program Lata group-distribution has the value $\log K_{ex} = 6.15 \pm 0.07$. The fluorescence of ZnR_2 at 544 nm upon excitation at 399 nm can be used for determining $0.1-1.2 \text{ } \mu\text{g Zn/cm}^3$ at pH 7.0-9.0. However several metals interfere seriously.	55

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
58.	Pyrocatechol-1-aldehyde-2-pyridylhydrozone	348 nm / 521 nm	5.5	-	This hydrazone reagent was prepared and its ionization constants spectrophotochemically determined. A procedure was developed for the fluorimetric determination of 12.250 ng/cm ³ of zinc in 50% vol./vol. Ethanol-H ₂ O medium, acetate buffered to apparent pH 5.5 (λ_{ex} = 398 nm; λ_{em} = 521 nm) using this reagent. Interferences were evaluated and the procedure was applied satisfactorily to the determination of zinc in potable tap water.	56
59.	Morin with Genapol PF-20	433 nm / 503 nm	4.7 $\pm$ 0.2	3 ng/cm ³	A method is described for the fluorimetric determination of zinc based on the formation of a Zn-morin complex in the presence of a non ionic surfactant. The complex has practically no fluorescence in the absence of surfactant, but the addition of Genapol PF-20 (non ionic surfactant, ethylene oxide-propylene oxide condensate) makes possible the fluorimetric determination of low concentrations of zinc as it enhances the fluorescence of the complex about 75 fold. Maximum fluorescence produced at pH 4.7 $\pm$	57

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
60.	1,5-bis (salicylidene-imino) quanine	390 nm / 450 nm	5.8	12.0 ng/cm ³	0.2(HOAc-OAc-buffer) with 1.5% surfactant and 0.009% morin. The fluorescence is excited at 433 nm and measured at 503 nm. The calibration graph is linear up to 150 ng Zn/cm ³ and the detection limit is 3 ng/cm ³ . The relative standard deviation (11 replicates) is 2.4% for zinc at 20 ng/cm ³ and 1.7% for 100 ng/cm ³ . Of 29 ions studied, Al(III), Be(II), Zr(IV) and cadmium(II) strongly increase the fluorescence of the system and Fe(III), Ni(II), Cu(II), Ti(IV) and Co(II) decrease the fluorescence signal.	58
					Zinc was determined fluorimetrically by reaction with 1,5-bis (salicylideneimino)quinidine in aqueous ethanolic solution at pH 5.8 to form a 1:1 complex. The fluorescence was measured at 450 nm upon excitation with 390 nm radiation. Beer's law was obeyed for 20-700 ng Zn/cm ³ . The detection limit was 12 ng/cm ³ . The effect of foreign ion was studied. The method was applied to determine zinc in pharmaceuticals.	

S. No	Name of the Reagents	$\lambda_{\text{ex}} / \lambda_{\text{em}}$	pH	Detection Limit	Remarks	Ref
61.	n-Octane sulphonate and 8-hydroxyquinoline	-	-	-	An HPLC method is developed for the determination of metals Zn (II), Ga (III), Y (III), In (III), Al (III), Zr (II), Cd (II) and Mg (II). An aqueous eluent containing n-octane sulphonate and weak organic acids were used to isocratically separate the mixtures of 11 metals on a SiO_2 -based C_{18} column. Secondary chemical equilibrium in the mobile phase governs retention, which is dependent upon stationary phase adsorption of metal detergent ion pairs and metal ligand complexes. Selectivity of the method is imparted by monitoring the fluorescence following post column reaction with 8-hydroxyquinoline. The detector response is linear for all metals and detection limits ranged from ppm to sub ppm levels for the different metals.	59
62.	1,5-Bis (2,3-dihydroxy phenylmethylene) thio carbonyl hydrozone	400 nm / 508 nm	6.5	-	The proposed reagent was synthesized by a standard reaction; its ionization constants are reported. A procedure is described for the spectrofluorimetric determination of the 5-540 ng Zn/cm^3 in 60/40-ethanol/water mediums, acetate	60

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					buffered to apparent pH 6.5 ($\lambda_{ex} = 400 \text{ nm}$, $\lambda_{em} = 508 \text{ nm}$). Interferences were evaluated and the procedure was applied with good results to the determination of zinc in portable waters ($0.3\text{-}3 \mu\text{g}/\text{cm}^3$) and lubricating oils.	
63.	Salicylaldehyde carbohydrozone (SACH)	-	6.5-5.8	$3.0 \text{ ng}/\text{cm}^3$	A method based on the reaction of zinc with salicylaldehyde carbohydrozone (SACH) was developed for the fluorimetric determination of micro gram amounts of zinc in solution. The reaction is carried out at pH 6.5-6.8 in 60% volume percent ethanol. The influence of reaction variables is discussed. The detection limit is $3.0 \mu\text{g}/\text{dm}^3$ and the range of application is $5\text{-}90 \mu\text{g}/\text{dm}^3$. The relative standard deviation of the method is 1.8%. The advantages of the proposed method include a high sensitivity of determination. Application to the determination of zinc in biological samples and alloys are discussed.	61
64.	Meso-tetrakis(4-hydroxyphenyl)	448 nm / 635 nm	8.3-9.6	$0.6 \text{ ng}/\text{cm}^3$	Zinc reacts with mesotetrakis(4-hydroxyphenyl)porphyrin[T-(4-HP)P] to form a 1:1	62

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	porphyrine[T-(4-HP)P].				complex over the pH range of 8.3-9.6 in presence of OP. The complexation is slow at room temperature; however it can be accelerated to completion within 5 minutes by heating the reactant mixtures in boiling water bath. The fluorescence is measured at 635 nm, with excitation at 448 nm. The calibration curve is linear over the range 0-1.3 $\mu\text{g Zn}/2.5\text{ cm}^3$ and the detection limit is 0.6 ppb. The proposed method was applied to the determination of zinc in tap water and hair with satisfactory results.	
65.	8-Hydroxy-quinoline-5-sulphonic acids with hexadecyltrimethylammonium bromide.	-	-	-	A method for the simultaneous determination of aluminium and zinc in their mixtures by first and second derivative synchronous fluorimetry is described. The method is based on the fluorescent complexes formed by aluminium and zinc with 8-hydroxyquinoline-5-sulphonic acids in the presence of hexadecyltrimethylammonium bromide as a surfactant. The range of application is between 0.02 and 0.10 $\mu\text{g}/\text{cm}^3$ for aluminium and between 0.1 and 1.0 $\mu\text{g}/\text{cm}^3$ for zinc. The accuracy and	63

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
precision of the method is reported.						
66.	Meso-tetrakis (3-N-methylpyridyl)porphyrin [T(3-MPy)P]	430 nm / 666 nm	8.7-9.7	1.0 ng/cm ³	Zinc (II) reacts rapidly with meso-tetrakis(3-N-methylpyridyl) porphyrin [T(3-MPy)P] to form a 1:1 complex over the pH range 8.7 to 9.7 at room temperature. The interference caused by remaining [T(3-MPy)P] can be eliminated by adding a small excess of copper(II) to form copper(II) complex. The fluorescence is measured at 606 nm after 0.5 hour of complexation with excitation at 430 nm at room temperature. The calibration curve is linear for 0-1.0 μ g Zn (II)/25 cm ³ ; the detection limit of the method is 1 ppb. The method established could be used for the determination of zinc (II) in tap water and hair.	64
67.	Ethioporphyrin II	λ_{em} : 578 nm	-	2.0 ng/cm ³	UV-Vis absorption at room and low temperature luminescence spectra of 8 reagents and their zinc complexes were examined. Ethiochlorophyll II was tested as an available reagent for determining zinc traces. The optimum conditions are: reaction with 10 ⁻⁵ M reagent in ethanol at 70-75°C for 10-15	65

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					minutes, measurement of luminance at 578 nm. The detection limit is $0.002 \mu\text{g Zn cm}^{-2}$. The effect of foreign ion was examined. Zinc $2.5 \times 10^{-7} \%$ was determined in high purity Hf with a standard deviation of 0.16 ($n = 5$).	
68.	Tetrakis (p-chlorophenyl) porphyrin	370 nm / 510 nm	7.0	-	Zinc was determined by fluorimetry based on the formation of 1:1 zinc: tetrakis(p-chlorophenyl)porphyrin in HCl-HOAc solution (pH 7) under the catalysis of ferrate reagent. The excitation and emission wavelengths are 370 nm and 510 nm respectively. The calibration curve is linear for $0-20 \mu\text{g Zn/25 cm}^3$. The method was applied to the determination of Zinc in ores and satisfactory results were obtained.	66
69.	Mesoleira (4-pyridyl) porphyrin(TPyP)	442 nm / 628 nm	acidic	-	The fluorescent complexing reaction of mesoleira(4-pyridyl) porphyrin(TPyP) with zinc(II) was investigated in acid medium. The excitation and emission wavelength of Zn (II)-TPyP complex are 442 nm and 628 nm respectively. The stabilization effects of various surfactants were	67

S No	Name of the Reagents	$\lambda_{\text{ex}} / \lambda_{\text{em}}$	pH	Detection Limit	Remarks	Ref
					examined, among which sodium dodecyl sulphate was the best. The fluorimetric method for the determination of trace zinc with TpyP was developed. The tolerance limits for more than 20 ions were over 100 times. The working curve is linear for 4-24 ng zinc/cm ³ . The method was applied to the determination of zinc in aluminium alloy with satisfactory results.	
70.	5,7-dichloro-2-methylquinolin-8-ol in Brij-35 micelle	-	-	3.0 ng/cm ³	A flow injection method is described for the determination of zinc in the range 10-600 µg/dm ³ , based on the fluorescence of the zinc-5,7-dichloro-2-methylquinolin-8-ol chelate in a Brij-35 micellar medium. The detection limit is 3 µg Zn/dm ³ and the sample throughput is 18 h ⁻¹ . The method was evaluated for the determination of zinc in pharmaceutical preparations and in tap water.	68
71.	Meso-tetra (p-trimethyl ammoniumphenyl) porphyrin [T(4-	-	basic	-	The determination of micro amount of zinc (II) by fluorescence has been studied based on complex formation of zinc (II) with Meso-tetra(p-trimethylammonium phenyl) porphyrin [T(4-	69

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
	TMAP)P ₃ with hydroxylamine hydrochloride.				<p>TMAP)P₃. The reaction proceeds in weak acid medium in the presence of the reductive agent hydroxylamine hydrochloride. When Zn-T(4-TMAP)P complex is decomposed by adding HCl, the fluorescence of released H₃P⁺ is determined. The fluorescence intensity is proportional to the concentration of zinc (II). The selectivity of the method was improved in comparison to single wavelength method. Three different mixed systems were examined with the method and satisfactory results were obtained.</p>	
72.	Salicylaldehyde benzoylhydrazine	380 nm / 460 nm	-	-	<p>A fluorimetric method for the determination of zinc through complexation with salicylaldehydebenzoylhydrazine is presented. The fluorescence excitation and emission wavelengths of the complex are 380 nm and 460 nm respectively. The molar ratio of zinc to salicylaldehyde benzoylhydrazine in the complex is 1:2. The selectivity of the proposed method is 4 ng/cm³. The contents of zinc in sodium chloride and sodium sulphate of AR grade reagent as well as calcium chloride of chemical grade</p>	70

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
reagents are determined with satisfactory results.						
73.	Salicylaldehyde-2-benzothiazolyl hydrozone	420 nm / 480 nm	8.6	3.0 ng/cm ³	A new fluorescence reaction of zinc with salicylaldehyde-2-benzothiazolylhydrozone was studied. The fluorescence excitation and emission wavelengths of the complex are 420 nm and 480 nm respectively. The reaction was carried out at pH 8.6 in an aqueous ethanol medium (50% vol/vol). The linear range 0-1.0 $\mu\text{g Zn}/10\text{ cm}^3$. The sensitivity of the method is 3.0 ng/cm ³ . The molar ratio of zinc to reagent is 1:2. The proposed method has been used for the determination of trace zinc in chemical reagents with satisfactory results.	71
74.	5-Formyl-3-hydroxy-4-hydroxymethyl-2-methylpyridine	-	-	104.0 ng/cm ³	A bifurcated fibre-optic sensor for Zn (II), Cd (II) and Ga (III) ions was fabricated. Chitosan modified with 5-formyl-3-hydroxy-4-hydroxymethyl-2-methylpyridine was immobilized on an agarose gel and used as a fluorogenic probe. The reproducibility of the response to zinc (II) was within 5% in 8 successive measurements at 5.0×10^{-5} M. A linear relationship with a correlation coefficient	72

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
75.	7-Iodo-8-hydroxy quinoline-5-sulphonic acid (Ferron) with hexadecyltrimethyl ammonium bromide	-	-	-	<p>of 0.999 was obtained in the Zn (II) concentration range of 0.20×10^{-5} M and the detection limit was 1.0×10^{-6} M ($S/N = 3$). Cd (II), Ga (III) were also detected, though sensitivities somewhat lower than that for Zn (II).</p> <p>The performance of Kalman filtering synchronous excitation and numerical derivative techniques for the resolution of overlapping emission spectra in spectrofluorimetry is studied. The extent of spectrum overlap was quantitatively described by the separation degree D_s, defined as the ratio of the peak separation to the full width at half maximum of the emission spectrum of the interferent. For the system of rhodamine B and rhodamine 6G with a large D_s of about 0.4, both Kalman filtering and synchronous techniques are able to resolve the overlapping spectra well and to give satisfactory results while the derivative spectra are still overlapped with each other. Moreover the sensitivities are greatly decreased in derivative techniques. For more closely spaced spectra</p>	73

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					emitted by the complexes of Al and Zn with 7-iodo-8-hydroxyquinoline-5-sulphonic acid (ferron)-hexadecyltrimethylammonium bromide, the synchronous excitation technique cannot completely separate the overlapping peaks, although it increases the separation degree from 0.025 in the conventional spectra to 0.37 in the synchronous spectra. On the other hand, Kalman filtering is capable of resolving this system, when the Al/Zn intensity ratio at the central wavelength of Al was >1. However the accuracy and precision of the estimation for zinc concentration produced by the Kalman filter become worse. In this event, the combination of synchronous excitation and Kalman filtering can much improve the analytical results.	
76.	N-Salicylidene aspartic acid (SASP)	271 nm / 448 nm	7.8-8.2	0.08 ng cm ⁻³	Fluorescent reaction of zinc with N-salicylidene aspartic acid (SASP) was studied. Zinc reacts with SASP to form a chelate in 10-25% ethanol-aqueous solution. The optimum pH range 7.8-8.2 and the maximum excitation and emission wavelength of	74

S. No.	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
77.	Cadmium- $\alpha, \beta, \gamma, \delta$ -tetra kis(4-sulphophenyl)porphyrin(H_2P^{4-})	422 nm / 604 nm	10-11	0.15 ng/cm ³	<p>the chelate are $\lambda_{ex} = 271$ nm and $\lambda_{em} = 448$ nm respectively. The fluorescence intensity is a linear function of the zinc concentration in the range of 0-2.5 $\mu\text{g}/25$ cm³ and the detection limit is 2.0 ng/25 cm³. Al (III), Ga (III), B₂ (II), Hg (II), Cd (II), Fe (II) and Cr (III) interfere with the determination of zinc, but the effect can be eliminated by extraction with dithizone. The method has been applied to the determination of Zn in environment water, wheat flour and human hair samples with satisfactory results.</p> <p>A highly sensitive spectrofluorimetric method for the determination of zinc was established by using the metal ion substitution reaction of the cadmium-$\alpha, \beta, \gamma, \delta$-tetra kis(4-sulpho phenyl)porphyrin (H_2P^{4-}) complex with zinc ion. The zinc complex Zn_2P^{4-} was quantitatively formed within 3.0 minutes at room temperature in the pH range 10-11. The acid dissociation constant (K_a) of $Zn_2P^{4-} + H_2O$ to form $[Zn(OH)P]^{3-} + H^+$ was calculated as $pH_1 = 13.2$; Zn_2P^{4-} is stable at pH 10-11. The relative</p>	75

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					fluorescence intensity ratio, $F(ZnP^{+})/F(CdP^{+})$ was 37.0 at $\lambda_{em} = 604$ nm ($\lambda_{ex} = 422$). The calibration graph was linear over the concentration range 5-100 ng $Zn(II)/cm^3$ in sample solution. The detection limit (signal-to-noise ratio = 3) was 0.15 ng $Zn(II)/cm^3$ and the relative standard deviation was 1.39% for 16.6 ng $Zn(II)/cm^3$ (ten determinations). Results are given for the application of the method to the determination of zinc (II) in tap water.	
78.	Amines with bis(salicylidene)ethylenediamine	340 nm 455 nm	9.5- 10.2	-	Zinc was determined in the presence of amines with bis(salicylidene)ethylenediamine hydrolysed in aqueous solution to liberate salicylaldehyde which reacts with the amine to form a schiff base. The zinc complex formed with the schiff base was stable in aqueous solution for 120 minutes. Aliphatic monoamines, eg isopropylamine had more intense fluorescence than diamines and aromatic amines. The zinc complex in the presence of isopropylamine has a blue fluorescence with an emission maximum at 455 nm and an excitation maximum at 340 nm. The optimum pH for the	75

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					fluorescence is at 9.5-10.2. The fluorescence intensity of the complex decreased gradually with increasing isopropylamine concentration beyond the optimum concentration (0.4-0.6), which is due to the masking of zinc by the excess amine. The range of the zinc determination with accuracy is 0.05-20 μg in 25 cm^3 .	
79.	2-Furaldehyde-2-pyridyl hydrazone (FAPH)	-	-	-	A sensitive and selective synchronous scanning derivative fluorimetric determination of zinc based on the formation of a fluorescent chelate with 2-furaldehyde-2-pyridylhydrozone (FAPH) is described and its analytical performance compared with that of the ordinary fluorimetric method. The detection limits lie in the ng/cm^3 range and the relative standard deviation is 2% in both the cases. The methods were applied to the determination of zinc in pig liver tissue and environmental fume samples.	77
80.	8-(benzenesulphonamido)quinoline	-	-	1.6 ng/cm^3	A chelating resin, 8-(benzenesulphonamido)quinoline immobilized on an XAD-7 support, was prepared	78

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
	on XAD-7.				and its use for the spectrofluorimetric determination of zinc and cadmium was studied. The immobilized material was placed in a flow cell in a spectrofluorimeter and used in a flow injection system. The fluorescent complex was formed and immobilized in the cell. The chelating resin could be stored for at least 3.0 minutes and used repeatedly without any appreciable amount of reagent being lost. Calibration graphs were linear up to 500 $\mu\text{g}/\text{dm}^3$ for zinc and 68 $\mu\text{g}/\text{dm}^3$ for cadmium. Detection limits can be improved by injecting larger volumes of sample. Preconcentration up to 10 was obtained for both metal ions.	
81.	Phosphate derivative of 1,2-dioxetane	-	-	-	A novel technique for the trace analysis of metal ions zinc (II), beryllium (II) and bismuth (III) in bulk solution is discussed. This technique involves the generation of a chemiluminescence signal from alkaline phosphatase catalysed hydrolysis of a phosphate derivative of 1,2-dioxetane. Zinc (II) can be determined by two methods, reactivation of the alkaline phosphatase apoenzyme and inhibition of	79

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					the native enzyme. Be (II) and Bi (III) can be determined quantitatively by inhibition of the native enzyme. Sub ppb to ppm level detection of zinc (II), beryllium (II) and bismuth (III) was achieved. Initial studies with mixed metals are also reported. The technique described is rapid and sensitive and can be readily applied to the micro assay of heavy metal ions.	
82.	N-Methyl-anthranilic acid (NMAA)	-	-	-	The effect of cations like Na (I), K (I), Cd (II), Cu (II), Ag (I), Zn (II), Co (II), Ni (II), Pb (II), Fe (III), Al (III) and Cr (III) on the fluorescence intensity of N-methylanthranilic acid (NMAA) was studied. All the cations studied with the exception of Na (I) and K (I) caused an enhancement in the fluorescence intensity of NMAA. Based on the fluorescence enhancement effect these cations were divided into three groups. The fluorescence enhancement phenomenon was used for spectrofluorimetric determination of these cations in aqueous samples. Limit of detection for each cation was also studied and reported.	25

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
83.	Dansylamide/apoc arbonic anhydrase	-	-	-	Fluorescence lifetime based chemical sensors have recently been described for applications in medicine, environmental monitoring and bioprocess control. These sensors transduce the level of the analyte as a change in the apparent fluorescence lifetime of an indicator phase. We have previously developed a wavelength-ratiometric fluorescence biosensor for zinc based on binding of zinc and dansylamide to apocarbonic anhydrase, which exhibited high sensitivity and selectivity. We demonstrate that the apocarbonic anhydrase/dansylamide indicator system is very well suited for life time based sensing with a sub nano molar detection limit and greater than 1000 fold dynamic range. The theoretical basis for the wide dynamic range is discussed.	80
84.	Bis-9-anthryl polyamide	λ_{em} : 495 nm	10.5	-	The use of metal promoted intramolecular excimer formation using a system derived from a simple linear polyamide is reported. The system demonstrates that considerably less preorganization is necessary than that used in cyclic systems. The	81

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
					water solubility results in the 1st aqueous operative radiometric fluoro sensor for Zn (II) ions, Bis-9-anthrylpolyamides were prepared by the 4 A molecular sieve promoted condensation of the polyamide with a stoichiometrically appropriate amount of 9-anthraldehyde in $CHCl_3$. These were titrated with Zn (ClO_4) ₂ in CAPS buffer (0.05M) at pH 10.5. The most notable feature of this titration is the nearly 4-fold increase in fluorescence intensity at ~495 nm. In fact, after the addition of 1.0 equivalent of zinc (II), the normal anthracene fluorescence profile is no longer the dominant feature of the spectrum. Subtracting the spectrum with no Zn (II) from that with 1.0 equivalent reveals the dominant excimer spectrum. The mono substituted control shows only the expected cheation enhanced fluorescence based upon the complexation state of the benzylicamine nitrogen.	
85.	Calcein blue (CB) in cetyltrimethyl ammonium	322 nm /440 nm	6.0	1.7 ng/cm ³	A fluorimetric method for the determination of zinc (II) in food based on the reaction of Zn (II) with Calcein blue (CB) to form a stable CB-Zn (II)	82

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	bromide				complex at pH 6.0 in the presence of cerium(IV) ammonium bromide to enhance the fluorescence intensity of CB was developed. The maximum excitation and emission wavelength of CB was 332 nm and 440 nm respectively. The linear range was 0.017-0.70 $\mu\text{g}/10\text{ cm}^3$ and the detection limit was 1.7 ng/cm ³ for Zn (II). The method was applied to the determination of Zn (II) in defatted milk powder, rice powder and Zn-fortified table salt with satisfactory results.	
86.	Peptidyl chemosensor	-	-	-	The design synthesis and characterization of a highly selective peptidyl fluorescent chemo sensor for Zn (II) are presented. This chemo sensor comprises a synhetic peptidyl template based upon a zinc finger domain and a covalently attached fluorescent reporter, which is sensitive to metal-induced conformational changes in the polypeptide construct. This approach combines the sensitivity of fluorescent detection with the remarkable carbon selectivity of the zinc fingers. The zinc sensor, ZnS, is capable of detecting nano molar concentrations	83

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
87.	Salicylaldehyde Thiocarbohydrozone with Triton X 100	-	-	5.0 ng/cm ³	<p>of Zn (II) in the presence of 50 mM Mg (II) and 100 μM Co (II), demonstrating the potential of this approach in environmental and biomedical applications. A modular synthetic approach was developed, which allows independent modification of the metal coordination sphere and the fluorophore for future construction of sensors for other metal cations.</p> <p>A room temperature flow injection spectro-fluorimetric method is presented for the determination of zinc (II) based on the use of salicylaldehyde thiocarbozone in the presence of Triton X-100 and sodium acetate-acetic acid buffer. Various physical and chemical variables affecting the reaction in the flow system were evaluated. The proposed method is very selective. The calibration graph is linear over the range 10-1000 ng/cm³ with a detection limit of 5.0 ng/cm³ and a relative standard deviation at the 50-ng/cm³ level of 1.8%. The method was successfully applied to the determination of zinc in drinking waters and</p>	84

S. No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
biological samples.						
88.	8-(benzenesulphonamido)quinoline	-	-	0.2 ng/cm ³	The development of a fluorimetric method for the determination of zinc, based on the fluorescence of the Zn-8-(benzenesulphonamido) quinoline chelate in a micellar medium of SDS is reported. The detection limit is 0.2 $\mu\text{g}/\text{dm}^3$, the working range 0.5-700 $\mu\text{g}/\text{dm}^3$ and the sample throughput is 145 h ⁻¹ . The method was evaluated for the determination of zinc in food and feed samples. A batch procedure for the simultaneous determination of zinc and cadmium based on the synchronous and derivative spectra is also proposed.	85
89.	Eosinate anion-crypland ethers with 1,2-dichloroethane	-	-	1.5 ng/cm ³	A highly sensitive and selective spectrofluorimetric method was developed for the determination of ultra traces of zinc based on solvent extraction with 1,2-dichloroethane of the ion-pair formed between eosinate anion and positively charged cryplate of zinc with crypland ethers. The detection limit for zinc is 1.5 ng/cm ³ , and the linear working ≥ 200 ng/cm ³ . The relative standard deviation is 1.8% at	86

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
90.	7-Iodo-8-hydroxyquinoline-5-sulphonic acid (ferron)	-	-	-	<p>the 100- ng/cm³ level. The proposed method was tested for the determination of zinc in coal and fly ash.</p> <p>The effect of different buffer systems, various surfactants and masking agents on the fluorescence characteristics of some metal complexes of 7-Iodo-8-hydroxyquinoline-5-sulphonic acid (ferron) were studied. A later-time resolved fluorescence method for the determination of zinc and aluminium was developed.</p>	87
91.	Salicylaldehyde-5-bromosalicyloyl hydrazone (SABSH)	393 nm / 465 nm	7.9	1.3 ng/cm ³	<p>A new fluorescent reagent SABSH was synthesized and the fluorescent reaction of this reagent with zinc was studied. Based on this chelation reaction, a fluorimetric method was developed for the determination of zinc in a 2-propanol-H₂O (1:1 v/v) medium at pH 7.9. Under these conditions the Zn-SABSH complex has excitation and emission maxima at 393 nm and 465 nm, respectively. The linear range of the method is 0-400 µg/dm³. The relative standard deviation of the method is 1.2%</p>	88

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					and the detection limit is $1.3 \mu\text{g}/\text{dm}^3$ of zinc when a standard addition method was used in the assay. The molar ratio of zinc to reagent is 1:2. Interferences of 36 other ions were studied. The method was successfully applied to the determination of trace zinc in wheat flour, rice, human urine and mineral water samples with satisfactory results.	
92.	1,2,4-Trihydroxyanthraquinone in ethyleneglycol and water	-	8.87	2.31 ng cm^{-3}	A new method for the spectrofluorimetric determination of zinc with 1,2,4-trihydroxyanthraquinone in a 80: 20(vol/vol) ethylene glycol-water medium at an apparent pH 8.87 provided by an ammonia/ammonium chloride buffer (pH 9.30) is proposed. The method allows the determination of zinc over the range $50\text{-}500 \text{ ng/cm}^3$ and features a detection limit of 2.31 ng/cm^3 . The influence of various chemical and physical variables affecting the reaction was evaluated and the effects of potential major interferences with the method are commented on. The proposed method has been successfully applied to the determination of zinc in	89

S. No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
several pharmaceutical preparations.						
93.	Stilbene fluo blue-S (2,2'-disulphonyl-4,4'-diaminostilbene- N,N,N',N' -tetraacetic acid disodium salt)	367 nm / 457 nm	6.0	-	Fluorescence quenching of the system containing Zn (II) and stilbene fluo blue-S (2,2'-disulphonyl-4,4'-diaminostilbene- N,N,N',N' -tetraacetic acid disodium salt) was studied. In a $H_3PO_4-H_3PO_3$ -HOAc-NaOH buffer solution (pH 6.0) the maximum excitation wavelength of stilbene fluo blue-S is 367 nm; the maximum emission wavelength is 457 nm. The formation of complex Zn (II) with the reagent causes the decrease of fluorescence intensity and is employed for the determination of trace zinc. The linear range is 0-0.8 $\mu g/10\text{ cm}^3$. The method was used for the determination of trace zinc in skim milk, human hair and nutrition table salt. The relative standard deviation was 3.4 for milk, 2.8 for human hair and 1.2 for table salt.	90
94.	Meso-tetrakis(4-methoxyphenyl) porphyrin in	-	-	-	Fluorescent spectra of super highly sensitive chelate systems containing multicomponent metal porphyrins are analysed by partial least square	91

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	Tween 80				method, and a computerized analysis for the simultaneous determination of Zn, Cd and Pb is developed. Zn, Cd and Pb quantitatively combine with meso-tetrakis-(4-methoxyphenyl) porphyrin in a strong basic medium and in the presence of Tween 80 when they are heated for 30 minutes in a boiling water bath. The proposed method was applied to the simultaneous determinations of Zn, Cd and Pb in artificial and environmental water samples and the recovery ratios are at 93.2-107%.	
95.	Ruthenium (II)- Terpyridine chromophore	-	-	-	The nearly non-luminescent ruthenium (II)-terpyridine chromophore, functionalized with an uncoordinated terpyridine fragment undergoes Zn (II)-induced association leading to a luminescent rod like 2: Zn (II): 2 species with luminescence enhancement factor $EF \geq 10$.	92
96.	1,10- Phenanthroline- H_2O_2 -NaOH with trimethylstearyl	-	-	-	A flow injection analytical technique along with chemiluminescence detection was studied to determine small amounts of zinc ions by the 1,10-phenanthroline- H_2O_2 -NaOH-system containing	93

S No	Name of the Reagents	$\lambda_{ex} / \lambda_{em}$	pH	Detection Limit	Remarks	Ref
	ammonium chloride (TSAC)				trimethylsilylammonium chloride (TSAC). This chemiluminescence method was based on the following reaction. The super oxide ion reacts with 1,10-phenanthroline to form a 1,2-dioxetane derivative intermediate, which emits chemiluminescence by way of an excited 3,3'-diformyl-2,2'-dipyridyl. Among the examined cationic surfactants, TSAC provided the highest enhancement of the chemiluminescence intensity, ~90-times higher than that in the absence of surfactants. The limit of the determination for Zn (II) was $2.5 \times 10^{-8} \text{ mol/dm}^3$ ($200 \times 10^{-6} \text{ dm}^3$ sample injection) under the optimum conditions. Also in the presence of 2,2'-bipyridine, the chemiluminescence intensity was enhanced nearly 5-times higher than that under the conditions without 2,2'-bipyridine. The authors studied the mechanism of chemiluminescence enhancement by spectrophotometry. The role of 2,2'-bipyridine was revealed through the 3-dimensional spectra of Zn (II)-1,10-phenanthroline complex formation, i.e. 2,2'-bipyridine enhanced the rate of chelate	

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
97.	N-(2'-pyridyl)-2-hydroxy benzamide (NPHB) in Brij-35 micelle	-	-	-	<p>formation on the Zn (II)-1,10-phenanthroline complex which was needed to produce the superoxide ion (anion radical). As a result, 2,2'-bipyridine increased the amount of superoxide ion and the chemiluminescence was enhanced.</p> <p>A sensitive spectrofluorimetric determination of Zn (II) with N-(2'-pyridyl)-2-hydroxybenzamide (NPHB) in Brij-35 micelle medium is described. The calibration graph is linear over the range 8-200 ng/cm³ with a regression coefficient of 0.997. Relative standard deviation was calculated at 0.050 and 0.150 $\mu\text{g}/\text{cm}^3$ and is 2.8% and 2.1% respectively. The method is relatively free from interference and was satisfactorily applied for the determination of zinc (II) in the samples of water and pharmaceutical samples.</p>	94
98.	Eriochrome blue-Black B	-	-	-	The interaction of zinc with eriochrome blue-black B was studied. The eriochrome blue-black B is immobilized on the modified sorbent Molsellect 72G-50 functioning as the sensitive layer of an	95

S. No.	Name of the Reagents	λ ex / λ em	pH	Detection Limit	Remarks	Ref
optical sensor.						
99.	5-Bromo salicylfluorone	365 nm / 538 nm	8.6	4.0 ng/cm ³	A method for the determination of trace zinc was presented based on the fluorescence-quenching effect of Zn (II) on 5-bromosalicylfluorone in pH 8.6 Na ₂ B ₄ O ₇ -HCl buffer medium. The excitation wavelength was 365 nm, the emission wavelength was 538 nm and the linear range 0-10 μ g/25 cm ³ and the detection limit 4.0 μ g/dm ³ . The interference of Fe (III), Cr (VI) and V (V) were masked by ascorbic acid and that of Co (II), Ni (II) and Pb (II) was by sodium citrate. The method was used in the determination of trace Zn (II) in H ₂ O and medicine samples with relative standard deviation 0.86%, the recovery 98.0%-101.5% and the results were consistent with those by polarography.	96
100.	2-methyl-8-(4-toluene sulphonamido)-6-quinolyloxy acetic acid, zinquin(I)	-	-	-	Zinc (II) specific fluorophores are of substantial importance in the study of intracellular Zn (II). Two such widely used fluorophores are 2-methyl-8-(4-toluene sulphonamido)-6-quinolyloxy acetic acid, Zinquin (I), and its ethyl ester, Zinquin ester	97

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
	and its Ethylester, Zincquin ester (2)				(2) which fluoresce strongly when bound by Zn (II). To gain insight into the factors affecting the fluorescence of such fluorophores the closely related 4-methyl-N-(6-methoxy-2-methyl-8-quinolyl)-benzene sulphon amide (3) and nine analogs (4-12), substituted at sulphur by nine different substituents have been prepared and their fluorescing characteristics and those of their Zn (II) complexes have been examined. The nine substituents are 2,2,2-trifluoroethyl (4), 4-methoxyphenyl (5), 4-acetamido phenyl (6), 4-bromophenyl (7), 4-nitrophenyl (8), 3-trifluoromethylphenyl (9), naphtha-1-yl (10), naphtha-2-yl (11) and 5-dimethylaminonaphth-1-yl (12). Under neutral conditions in 75/25% vol./vol. Ethanol/water solutions, (3)-(7) and (9)-(11) fluoresce weakly in the free state; (8) does not fluoresce and (12) fluoresces strongly. UV-Vis spectroscopy shows that (3)-(12) complex to Zn (II), but unlike the remainder, the complexes of (8) and (12) do not fluoresce, with those possessing electron withdrawing substituents (4) and (9), being	

S No	Name of the Reagents	λ_{ex} / λ_{em}	pH	Detection Limit	Remarks	Ref
					the most fluorescent. On this basis ethyl-2-(2-methyl quinolyloxy)-8-(2,2,2-trifluoroethylsulfonamido) acetate (19) was prepared and its Zn (II) complex was found to be substantially more fluorescent than that of (2).	

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